



TITLE:

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CITATION:

Takada, Toshio ...[et al]. Preparation and Properties of New Ferrous Basic Sulfate. Bulletin of the Institute for Chemical Research, Kyoto University 1969, 46(6): 295-299

ISSUE DATE:

1969-03-31

URL:

<http://hdl.handle.net/2433/76254>

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Preparation and Properties of New Ferrous Basic Sulfate

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Received October 15, 1968

A new ferrous basic sulfate has been found in the course of neutralizing ferrous sulfate solution by NaOH aqueous solution and its chemical composition as well as its crystal structure has been determined. Some anomalous magnetic properties of this salt have been studied.

I. INTRODUCTION

Many papers have been published on the neutralization of ferrous sulfate aqueous solution with alkaline solution. According to the previous literatures, only one kind of ferrous compound $\text{Fe}(\text{OH})_2$ was precipitated, when an excess amount of the alkaline solution was added to the solution containing ferrous ions. When an insufficient amount of alkaline solution was added to the ferrous sulfate solution, ferrous hydroxide precipitated at first, and then it was converted to the so called "ferrous basic salt". This basic salt was composed of ferrous sulfate and hydroxy ions. Feitknecht *et al.*⁽¹⁾ made a detailed investigation on the ferrous basic salts obtained from the ferrous chloride solution and found three kinds of basic salts. Further, he found⁽²⁾ that the ferrous basic salt containing SO_4 ions is $3\text{Fe}(\text{OH})_2 \cdot \text{FeSO}_4$ in chemical composition and hexagonal in structure type.

In the course of our experiments another ferrous basic sulfate, which was different from the above salt in chemical composition and crystal structure, was found to form, when the ferrous sulfate solution was neutralized with the NaOH solution. In this paper, the preparation method and some magnetic properties of this new ferrous basic sulfate are reported.

II. EXPERIMENTAL AND RESULTS

1. Preparation of Sample

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH and H_2SO_4 of analytical grade were used as starting materials. Oxygen free water was prepared by boiling distilled water for more than 15 hr with passing of nitrogen gas in it and then cooling it down to the room temperature. Ferrous sulfate solution was prepared by dissolving 500 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 2 l of 0.125 N- H_2SO_4 solution contained in a 3 l flask and alkaline solution was prepared by dissolving 82 g of NaOH in 1 l of oxygen free water. NaOH solution was added to ferrous sulfate solution, while nitrogen gas was passed in it to prevent the ferrous ions from oxidation. The reaction vessel is shown schematically in Fig. 1. The flask was placed in a mantle heater and the solution was maintained at 70°C for 20 hr. Nitrogen gas was passed in the solution for prevention of oxidation and as agitator. The following reaction was observed. At the first stage of the

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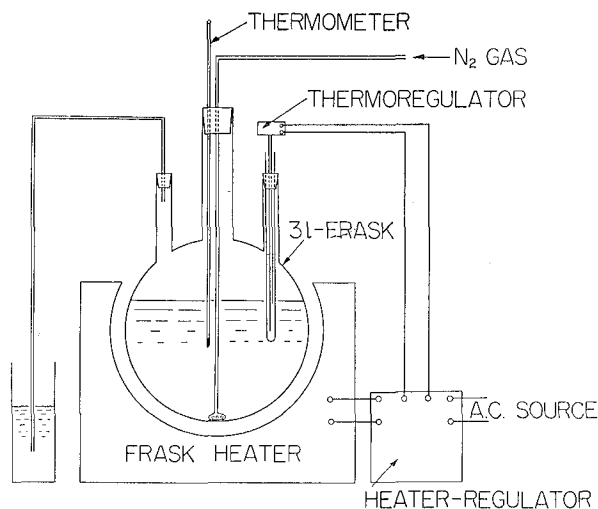


Fig. 1. Apparatus for preparation of the ferrous basic sulfate.

reaction, white precipitate of ferrous hydroxide was formed and changed quickly into colloidal suspension. At the second stage the colloidal precipitate gradually disappeared and new white precipitate appeared. This new precipitate was submitted to the following examinations.

2. Chemical Composition

All procedures for chemical analysis of the sample were performed in nitrogen gas atmosphere, because the wet precipitate thus obtained was easily oxidized in the air. The precipitate was filtered and then dried in a desiccator. The ratio of the content of the iron ions to the sulfate ions in the sample was determined to be 5:1 by usual chemical analysis. Sodium ions were not detected. The iron ions were found to be divalent by the potassium thiocyanate method. This was also confirmed from the value of quadrupole splitting of Mössbauer spectrum at liquid nitrogen temperature where paramagnetic state was observed. The results obtained were summarized in Table 1. These data show that the compound consists of Fe^{2+} , SO_4^{2-} , and H_2O . Therefore the chemical formula of the compound seems to be $3\text{Fe}(\text{OH})_2 \cdot 2\text{FeSO}_4$.

Table 1. Analytical result of the ferrous basic sulfate.

Component	Fe^{2+}	SO_4^{2-}	Fe^{3+}	Na
	41.06	27.26		
Weight percent	41.56	28.94	<0.4	0
	41.39	28.19		
Average value	41.33	28.13		
Mole ratio	2.53:1			

3. Crystal Structure

The crystal structure was determined by x-ray powder method using Fe-K α radiation. Peak positions were determined with usual fixed count method and using ZnO and MgO as reference substances. X-ray pattern of this compound closely resembled to that of Fe(OH) $_2$ ·FeOOH, whose crystal structure was determined to be hexagonal by Bernal *et al.*³⁾ Therefore, the crystal structure of the compound was confirmed to be hexagonal with calculated lattice constants: $a=3.24$ Å and $c=10.2$ Å. The hexagonal structure of this compound was also indicated by the electron diffraction pattern shown in Fig. 2.

Table 2. X-ray diffraction data for the ferrous basic sulfate.

d (Å)	I/I_0	(hkl)
10.2	50	0001
5.1	100	0002
3.4	70	0003
2.81	5	10 $\bar{1}$ 0
2.55	25	0004
2.04	5	0005
1.70	8	0006
1.618	5	11 $\bar{2}$ 0
1.456	5	0007
1.272	5	0008

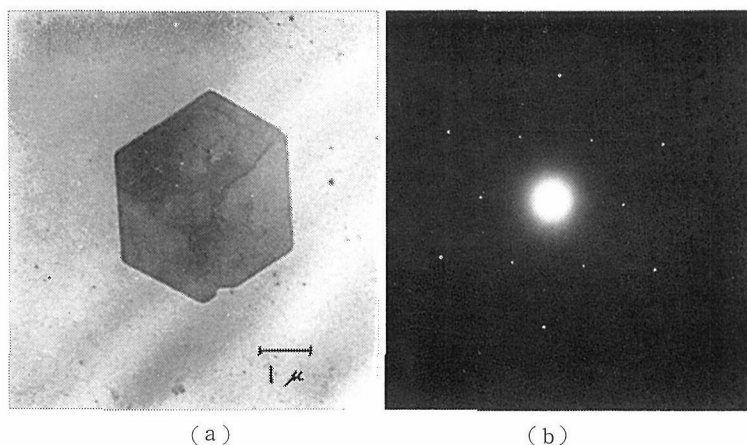


Fig. 2. (a) Electron micrograph of the ferrous basic sulfate.
(b) Electron diffraction pattern of the ferrous basic sulfate. Electron beam enters in the direction perpendicular to the (0001) plane of the crystal.

4. Magnetic Properties

Magnetic susceptibility was measured with A-C Hartshorn bridge in the temperature range from 1.2°K to 77°K. The frequency of 35 c/s was used. Magnetiza-

tion was measured using Cioffi type recording flux meter and superconducting magnet with the field up to 45 KOe at liquid helium temperature. Calibration of search coil was made with nickel metal powder. Magnetic susceptibility versus temperature curve is shown in Fig. 3. This compound seems to have two magnetic transition points of 5.4°K and 8.5°K. Above the magnetic transition temperature

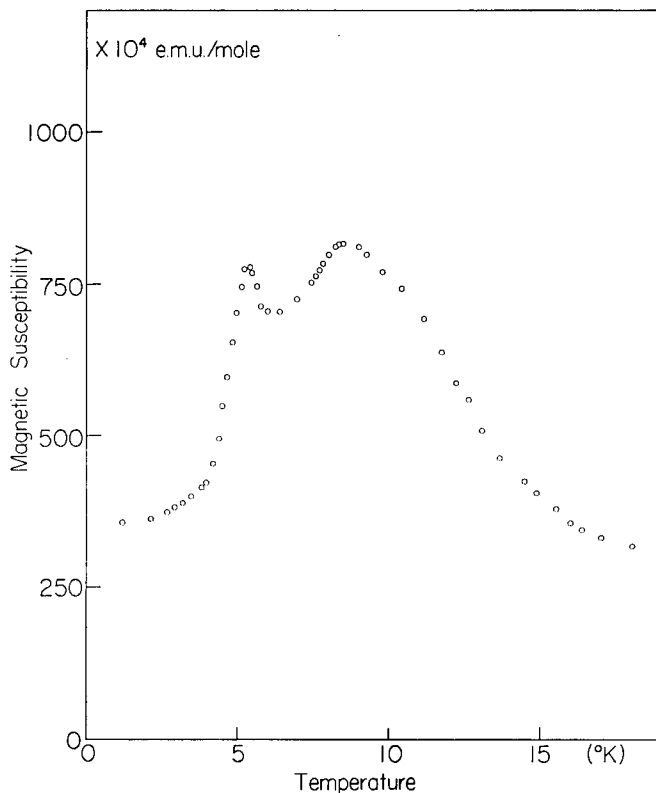


Fig. 3. Temperature dependence of magnetic susceptibility of the ferrous basic salt.

the magnetic susceptibility obeys the Curie-Weiss law. This compound is considered to be an antiferromagnetic substance. The transition peak of the higher temperature is round and that of the lower temperature is sharp. Maximum peak values are 755×10^{-4} e.m.u./mol and 763×10^{-4} e.m.u./mol, respectively. These magnetic properties also indicate that this compound is the new kind of basic iron sulfate. From the crystal structure of this compound and the temperature dependence of magnetic susceptibility, it may be expected that in this compound two dimensional antiferromagnetic ordering occurs presumably in *c*-plane at the higher transition temperature because of the strong anisotropy in superexchange and then three dimensional magnetic ordering occurs at the lower transition temperature. Further study on this point is in progress. Magnetization curve is shown in Fig. 5. The field dependence of the magnetization changed at the magnetic field of 30 KOe. This point may signify a certain transition of spin state.

New Ferrous Basic Sulfate

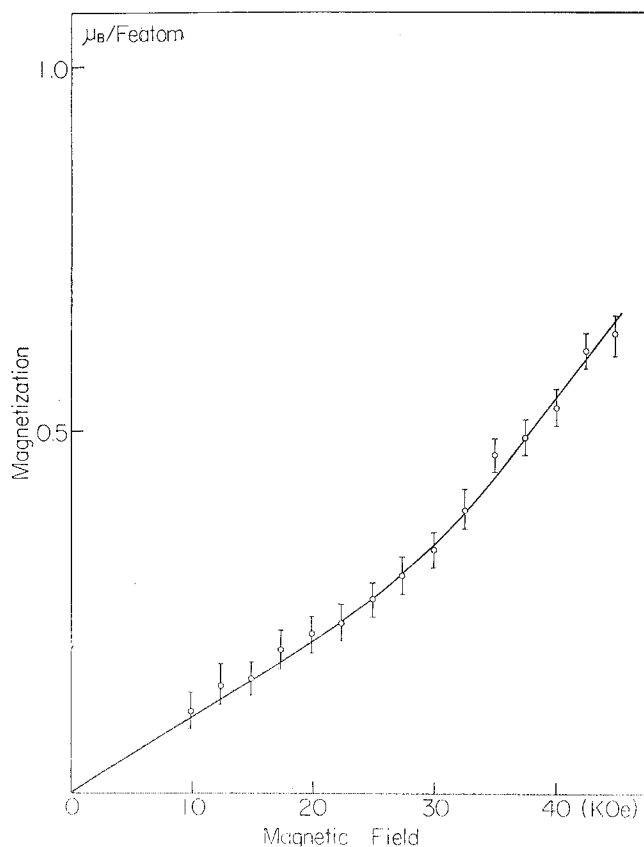


Fig. 4. Field dependence of magnetization of the ferrous basic salt.

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